



Memorandum

*To: Charlie Coleman, EPA
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*From: Gunnar Emilsson, CDM Smith
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Date: November 18, 2014

*Subject: Response to Comments, EnSci, Inc. Memorandum of June 22, 2014 entitled
Technical Memorandum and Response ARWW&S Arsenic Source
Investigation; Final Project Data Summary Report, dated 10-31-2013; CDM
Smith, April 9, 2014*

General Comments

EPA had asked CDM Smith to provide an interpretive report (CDM Smith 2014) applying the new information gathered by the MBMG at the Anaconda Smelter NPL Site (the site) since October 2013 to refine the existing conceptual site model (CSM) for arsenic concentrations in ground water at the site. EPA now requests CDM to provide this response to comments by Atlantic Richfield and its consultants on the interpretive report.

This response to comments centers on a series of documents issued for the site. Those documents are:

- **October 31, 2013.** ARWWS Arsenic Source Investigations, Final Project Data Summary Report, prepared by the Montana Bureau of Mines and Geology (MBMG) for Atlantic Richfield.
- **December 2013.** Draft Arsenic Source Investigation Interpretive Analysis Report, prepared by Atlantic Richfield.
- **February 2014.** Agency General Comments – Draft Arsenic Source Investigation Interpretive Analysis Report dated December 2013 (Atlantic Richfield) and ARWWS Arsenic Source Investigations Data Summary Report (MBMG).
- **April 9, 2014.** Agency Interpretive Report for MBMG's ARWW&S Arsenic Source Investigation Final Project Data Summary Report, prepared for the U.S. Environmental Protection Agency (EPA) by CDM Smith.

- **June 24, 2014.** Letter from Davis Graham & Stubbs (DGS) on behalf of Atlantic Richfield containing comments by EnSci, Inc. (EnSci) on the April 9, 2014 agency interpretive report prepared by CDM Smith.

The existing CSM was developed collaboratively by Atlantic Richfield and the Agencies over the past 25 years in such documents as: Anaconda Regional Soils Operable Unit Remedial Investigation Report (Atlantic Richfield 1996a) and Anaconda Regional Water and Waste Operable Unit Remedial Investigation Report (Atlantic Richfield 1996b). These documents support the site characterization summarized in the Anaconda Regional Water Waste and Soils Operable Unit (ARWW&S OU) Record of Decision (ROD) (EPA 2009), which led to the bedrock aquifer technical impracticability (TI) waiver identified in the ROD. Subsequent additional characterization of ground water and lowering of the arsenic drinking water standard necessitated amendment of that ROD in 2011. That 2011 ROD amendment added two new alluvial-aquifer TI zones and expanded the existing bedrock-aquifer TI zone in areas where leaching of arsenic from surface soils resulted in exceedances of the drinking water standards. The 2011 ROD amendment also acknowledged that there is potential for naturally-occurring sources of arsenic in ground water to be present in and near the site.

Atlantic Richfield's interpretive analysis report (Atlantic Richfield 2013) offers a radically different CSM that limits the area in which water may be considered to be impacted by smelter emissions (>10 $\mu\text{g/L}$ arsenic performance standard) to a distance of less than 6 miles from the stack and a maximum depth of 35 feet. Outside of waste management areas, the primary source of arsenic in ground water in this proposed CSM is the circulation of geothermal waters over broad areas of the site. Agency acceptance of this alternative CSM would require development of a new ARWW&S OU ROD amendment that identifies significantly smaller TI zones, as areas impacted by naturally-occurring arsenic would be excluded from CERCLA TI waivers. Because existing data show no direct correlation between arsenic and ground water temperature (geothermal waters), the basis of such an amendment would be solely the conclusions of Atlantic Richfield's interpretive report.

As noted in the EnSci comments of June 22, 2014, both Atlantic Richfield and the Agencies agree that mineralized rock in the English Gulch and Crackerville areas may provide a source of naturally-occurring arsenic in ground water in those areas, although an accurate method of distinguishing between naturally occurring and smelter-related arsenic sources in a given supply of ground water has not been identified. Atlantic Richfield and the Agencies disagree on the following:

- Atlantic Richfield maintains that smelter emission impacts from ground water are limited to less than 6 miles from the stack and to a depth of 35 feet. The Agencies do not agree.
- Atlantic Richfield maintains that geothermal waters are the source of elevated arsenic and are found in many areas beyond the Fairmont and Warm Springs locations. The Agencies do not agree.

As discussed in the Agency comments (CDM Smith 2014) to the Atlantic Richfield interpretive report (AR 2013), the fundamental flaw of the statistical analysis done by Atlantic Richfield was the

use of temperature differences of as little as one half degree Celsius as the key parameter for developing arsenic clusters. Temperature is affected by too many variables for temperature data to serve as a basis for developing clusters/ground water classifications. Factors such as the increased heat in wells caused by submersible pumps, springs/seeps sampled in different weather events, etc., all affect temperature accuracy. Ground water classifications should therefore not be based on small variations in temperature data.

The effects of this erroneous classification process can be seen by examining the maps showing the 20 classifications in Figures 18 through 25 of the interpretive report. Fairmont and Warm Springs/Geyser Gulch geothermal waters are randomly assigned across the site (note that Geyser Gulch water has arsenic concentrations less than the arsenic drinking water standard). A spring east of the Warm Springs Ponds, with arsenic concentrations less than the arsenic drinking water standard, is assigned to the Opportunity Ponds waste group family, even though there are no mining wastes anywhere near this location (Figure 22). Smelter emissions impacted waters are limited to only 2 groups out of 20, indicating that Atlantic Richfield developed their 6-mile cutoff by ignoring the existing database of spring/seep data used to characterize TI zones in the 2011 ARWW&S OU ROD amendment.

A cursory review of the 280 samples used by Atlantic Richfield to complete the geostatistical analysis and their assigned group classification provides two examples that illustrate the flawed nature of the analysis in the interpretive report.

- **Failure to account for differing arsenic concentrations with depth.** At a nested pair of monitoring wells (wells at the same location but screened at different depths) on Smelter Hill, the arsenic concentration in the 125-foot deep well (MW-245s) is 915 µg/L while the concentration in the 214-foot deep well (MW-245e) is 18 µg/L. This decrease in concentrations with depth is consistent with the existing CSM for impacts from smelter emissions (e.g., leaching of arsenic in surface soils impacts the uppermost aquifer). In contrast, the interpretive report classifies both wells as Warm Springs/Geyser Gulch geothermal waters, ignoring the difference in concentrations between the two depths.
- **Differing classifications of geothermal waters in a single location.** At nested well pair MW-249, the 19-foot deep well (MW-249s) has an arsenic concentration of 39 µg/L and is classified as Warm Springs/Geyser Gulch geothermal water, while the 205-foot deep well (MW-249d) has an arsenic concentration of 4.3 µg/L and is classified as Fairmont geothermal/volcanic interaction water. The interpretive report does not explain how two different types of geothermal waters would exist at the same well location.

By limiting the sample set of well and spring/seep water assigned to smelter emissions to a very narrow set of data, while erroneously assigning the remaining sample sets to geothermal sources based on the use of unreliable temperature data to extrapolate correlations, Atlantic Richfield produces an unsound interpretation of ground water geochemistry at the ARWW&S OU.

In response to Atlantic Richfield's comment that CDM Smith ignored critical geothermal constituents in their analysis, an Addendum to the Agency Interpretative Report has been prepared and is attached to this response to comments. CDM Smith evaluated five trace elements (tungsten, boron, lithium, rubidium, and cesium) which were identified by Atlantic Richfield as being important indicators of geothermal activity, and consequently elevated arsenic concentrations in ground water. As discussed in the Addendum, our analysis indicates that these trace elements have multiple potential sources within the study area, and the only source containing significant leachable arsenic was hydrothermal alteration of bedrock as observed at Crackerville and English Gulch core drilling sites. As noted in the Addendum, it appears that Atlantic Richfield's practice of interchanging the terms "hydrothermal" and "geothermal" has resulted in some misunderstanding of the existing Site ground water data and the Agencies' technical interpretation of that data.

Specific responses to the six comments in the EnSci review of the Agency Interpretive Report for MBMG's ARWW&S Arsenic Source Investigation Final Project Data Summary Report, as summarized in the DGS letter, are provided below.

Specific Comments

EnSci comments are provided below in italicized text followed by the CDM Smith response.

AR Comment

1) The CDM Report's Biased Data Interpretation

Notwithstanding the fact that the geostatistical classifications performed by Atlantic Richfield were statistically significant, the CDM Report ignores critical geothermal constituents and their chemistry in their entirety. This is a fundamental bias of the report that renders its conclusions unreliable.

CDM Smith Response

As identified in the Agencies' comments to AR's Interpretive Report, the geostatistical classifications performed by AR are clearly flawed. As stated on page 1 of AR's interpretative report, "a multiple regression analysis predicted regional geothermal As concentrations with an adjusted R² of 0.79 (describes 79% of the variability of As concentrations) with groundwater temperature being the most important variable in explaining relationships among data (i.e., the single regression parameter that explains the most variability)". The points that the Agencies made concerning the induced temperature correlation were:

1. Temperature data are too subject to error introduced from time of year of collection, the time of day, and sunlight conditions affecting springs/seeps, to submersible pump motors warming domestic wells, to allow temperature clusters based on 0.5 degrees Celsius differences to be meaningful.
2. Identified geothermal waters within the southern Deer Lodge valley (e.g., Fairmont (Gregson) and Warm Springs) are very narrow hot water vents along permeable fault zones

with very little temperature gradients observed beyond the initial uprising of warm water, as that water is soon diluted by much greater volumes of colder waters influenced by atmospheric conditions.

3. There is no evidence of significant geothermal-related mineral precipitation beyond the narrow geothermal corridors of warm water upwelling associated with the known geothermal areas at the site. Hydrothermal alteration associated with late Cretaceous – early Eocene (which occurred more than 50 million years ago) batholithic intrusive and volcanic extrusive events, which were the source of arsenic and other trace elements detected in MBMG's rock core analysis at Crackerville and English Gulch, are unrelated to late Cenozoic deep fault circulation of geothermal waters that occur at the present time.

The Agencies' prior comments include graphs and other supporting information rejecting the AR assertion that widespread geothermal waters (that are a significant source of arsenic in water) are present in the southern Deer Lodge valley.

In response to the comment that critical geothermal constituents have been ignored, as noted above, CDM has prepared the attached Addendum setting forth additional analyses of these constituents. These analyses reveal no evidence of widespread trace element distribution that correlates to the Site TI zones, nor do they provide any basis for departing from the CSM conclusion that smelter deposition is the primary source of arsenic concentration in the TI zones.

AR Comment

2) The CDM Report Incorrectly and Inconsistently Interprets Key Data

The CDM Report's statement that, "Groundwater arsenic concentrations varied across the site in a fairly predictable manner, at least for concentrations above about 20 µg/L" is incorrect and not supported by the data. See CDM Report at 2-1 to 2-2. Further, the report's implication that arsenic exceedances above 20 µg/L throughout the ARWW&S are related to former smelter emissions is also incorrect and not supported by the data.

CDM Smith Response

AR appears here to reject the hypothesis that mining and smelter related impacts decrease away from the smelter over distance. Yet decreases in groundwater arsenic concentrations with distance from the stack are acknowledged and illustrated at pp. 9-10 and Figures 26-27 of AR's interpretive report. The referenced Figure 2-1 presented in CDM's interpretive report shows that the decline in groundwater arsenic concentrations with distance from the stack would be expected to hold true for wells located downwind from the stack and for arsenic concentrations exceeding 20 µg/L.

Had CDM examined the voluminous MBMG chemistry data for the samples that form the so-called "predictable trend," they would have identified at least five very different groundwater populations having very different origins. Three of these include shallow groundwater populations associated with

arsenic-bearing mining waste (two from Opportunity Ponds) that have no association with areal smelter deposition.

The “key data” Atlantic Richfield contends that CDM ignores refers to the “five very different groundwater populations having very different origins” mentioned by EnSci (EnSci Memorandum at 2). These populations were identified through the flawed statistical analysis based on unsound temperature data analyzed in our previous comments to the Atlantic Richfield interpretive report and the response to Comment 1 above. As a result, Atlantic Richfield improperly associates certain groundwater populations with the Warm Springs Hospital/Geyser Gulch and Fairmont geothermal waters even when these groundwaters are some miles away and upgradient from these known geothermal waters. Figures 18 and 19 of the AR Interpretive Analysis Report depict extensive geothermal waters throughout the Site on the basis of this flawed statistical analysis.

CDM Smith did not state that arsenic exceedances above 20 µg/L in groundwater are solely due to smelter emission deposition in soils, as we acknowledge the highest levels of arsenic concentrations in ground water likely have significant contributions from smelting/mining wastes deposits from the Smelter Hill/Opportunity Ponds WMA. Of course, differentiating groundwater arsenic loads traced to historic leaching of flue dusts from arsenic resulting from smelter emissions is as difficult as distinguishing relative contributions of arsenic from smelter emissions and naturally occurring arsenic.

AR Comment

3) *The CDM Report Mischaracterizes Differentiating Sources of Sulfur Dioxide*

The CDM Report misrepresents and artificially characterizes the $\delta^{34}\text{S}$ range for “smelter fallout and abiotic sulfide”. The upper $\delta^{34}\text{S}$ limit in the CDM Report is unjustified and falsely represents the actual data and the report provides no supportable rationale for extending the range. As a result, the report’s conclusion that “[I]n general it is not possible to differentiate between sulfur dioxide fallout from smelters and other industries from leaching of abiotically-formed sulfides” is not accurate, reflective of the data, and should not be relied upon for purposes of evaluating groundwater chemistry in the anaconda area.

CDM Smith Response

Despite this criticism, AR cites the same $\delta^{34}\text{S}$ value in its own analyses (AR Interpretive Analysis at 7; EnSci Memorandum at 3 (sixth bullet)). The EnSci reviewer apparently thought that the hydrothermal alteration reported in the Crackerville Core, with a $\delta^{34}\text{S}$ value of +14.3‰ (as well as leaching 522 µg/L arsenic) is the result of geothermal waters. As the attached Addendum explains, the difference between hydrothermal alteration, which occurred in the Butte/Anaconda area millions of years ago, and current geothermal activity is important.

The upper $\delta^{34}\text{S}$ limit of 14‰ for smelter fallout and abiotic sulfide used by the CDM Smith report is indeed justified by the data. EnSci cites a 1966 study of $\delta^{34}\text{S}$ values for Butte ore for 21 samples as

a basis that “the Anaconda smelter emissions and mining waste should range between -3.6 to +4.1 (based upon Butte porphyry ore)”. This study, however, is superseded by a more recent 2005 study by the same author that includes much higher $\delta^{34}\text{S}$ values for several minerals (especially the sulfates) within the Butte ore body, which are consistent with the Crackerville data (Field et al 2005; available at <http://digitalcommons.unl.edu/usgsrve/12/>). The sulfates would have been roasted at the early stages of the copper smelter process, and consequently high $\delta^{34}\text{S}$ would be likely.

The Agencies do not dispute that locally, mineralized rock contributes to arsenic concentrations in ground water. This mineralization likely occurred during the late Cretaceous to Eocene time, and has no association with geothermal waters that are more associated with deep circulation along late Cenozoic faulting. The analysis in the CDM Smith report was attempting to determine if $\delta^{34}\text{S}$ could be used to differentiate between mining and smelting sulfate and naturally occurring sulfate. As the report notes, “smelter fallout is not the only source of sulfate in the groundwater or post depositional reactions have occurred which have masked the $\delta^{34}\text{S}$ vs. distance relationship.”

AR Comment

4) *The CDM Report Ignores Fundamental Geothermal Tracer Constituent Data*

Many other groundwater constituents besides $\delta^{34}\text{S}$ are associated with geothermal activity (and arsenic sourcing). These include suites of hydrothermal metals, REE, and anions (W, Cs, Rb, Li, B, F, Pd, Tl, Hg, As, etc.; Barnes, 1974). The CDM Report does not consider this available MBMG data. In fact, the CDM Report did not evaluate a single geothermal indicator from the MBMG core analyses, the core leachate analyses, the soil leachate analyses, the hot geothermal vent water from the known geyser mounds, or the ARWWS&S groundwater itself. The leachate results show strong correlations between the classic geothermal indicators (W, Rb, Cs) and arsenic in the Powell Vista (MS) core and the Fairmont (FR) and Crackerville (SH) cores. This is a fundamental flaw of the CDM Report.

CDM Smith Response

See discussion in the attached Addendum, as well as the response to Comment 1 regarding the geothermal constituents. The attempt to connect geothermal source waters to W, Rb, and Cs concentrations in rock core leachate is puzzling. Rock core leachate is clearly sourced from the rock itself and not geothermal waters.

The identification of the arsenic source within the Powell Vista groundwater to either smelter fallout or bedrock sources, and not geothermal sources is well supported. Surface soils in the Powell Vista area leach at least 450 $\mu\text{g/L}$ arsenic, and this is from a soil with a total arsenic content of only 145 mg/kg. Previous arsenic concentrations in surface soils in the Powell Vista/Launderville area ranged from 200-450 mg/kg. Had these samples been subjected to leaching tests, the arsenic concentrations in the leach solutions would likely be much higher than 450 $\mu\text{g/L}$. Tritium data clearly indicate that 1950s era water is present at depths of over 300 ft. at Powell Vista/Launderville. The presence of very leachable arsenic in surface soil and its pathway through

the unsaturated zone to the groundwater table in the Powell Vista/Launderville area are both well illustrated. To attribute the arsenic in the Powell Vista/Launderville area groundwater solely to geothermal sources which are known to contain less than 30 µg/L arsenic is unsupported.

The rock core from the deep well at Crackerville (119 meters) leached 522 µg/L arsenic. Clearly, the arsenic at this depth is not from geothermal waters but is derived from the local mineralized bedrock.

Arsenic is present in the surface soils at Fairmont at a concentration of 165 mg/kg which leach over 200 µg/L arsenic. This suggests that smelter emissions, instead of a geothermal source, are likely the most prevalent source for the arsenic in shallow groundwater there.

AR Comment

5) *The CDM Report has Significant Flaws in Assessing Arsenic Trends at Depth*

The CDM Report utilizes leachate arsenic concentrations measured on the upper six inches of surface soil to assess arsenic trends at depth. This method is technically suspect and has no bearing on the actual downward flux of arsenic. The CDM Report's soil analysis failed to include basic soil mineralogical analysis, measurements of soil surface area, determination of ion exchange capacity, soil pH measurements, or selective extraction determinations, among others. For these reasons, the report's conclusions regarding the origin of arsenic in ARWW&SOU groundwater are not technically supportable.

CDM Smith Response

The flux of arsenic from the surface soils to groundwater at depth is supported by the arsenic leaching data of the surface soils and the fact that the path of infiltration water is through the vadose zone. That relatively young waters are present at depths of 300 feet is supported by the tritium data. Further characterization of the surface soils (pH, sequential extractions, etc.) will not change the fact that they are very leachable in terms of arsenic.

Where monitoring well nests are present in areas impacted by smelter emissions (e.g., Smelter Hill and Stucky Ridge), the data show that arsenic concentrations are invariably higher in the shallow well than in the deeper well, consistent with the CSM of smelter emissions being the primary source of arsenic in the ground water. Under the geothermal waters model, arsenic concentrations should increase with depth. AR is invited to test their model in the Powell Vista area by designing a ground water investigation to determine the arsenic concentrations in shallow, intermediate, and deep ground water in order to resolve this issue. Note that as there is likely naturally occurring arsenic at depth in the Lowland Creek volcanics in the Crackerville area, such a shallow to deep investigation would likely not yield any conclusive data in that area. The lack of a clear indicator constituent associated with smelter emissions-derived arsenic in ground water is a significant impediment to distinguishing naturally occurring arsenic from arsenic caused by smelter fallout in this area.

The monitoring well nest data is also useful in reviewing AR's assertion that "the smelter As signature is limited distally (6 mi) and vertically (<35 ft. bgs) while the natural geothermal As exhibit >10 ug/L signature is pervasive throughout the DWAOC" (page 2, AR Interpretative Report). As previously discussed, the 125-foot deep well (MW-245s) has an arsenic concentration of 915 µg/L while the concentration in the 214-foot deep well (MW-245e) is 18 µg/L. Not only is 125 feet far deeper than the AR suggested limit of 35 feet, the decreased As concentration at the depth of 214 feet is consistent with the "top-down" CSM of smelter impacts, compared to the "bottom-up" theory of geothermal impacts.

The existing data, where available, contradicts AR's statistical interpretation of a 35 feet below ground surface limit on arsenic impacts from smelter emissions, particularly in bedrock aquifer settings. The wells used in the Bedrock Aquifer TI evaluation were in upland areas known to have soil contaminated solely from smelter emissions fallout. In these areas, arsenic is found in ground water down to at least 201 feet below ground surface 2.7 miles south from the stack at Cabbage Gulch, 63 feet below ground surface 3.6 miles southwest from the stack at Joyner Creek, and 182 feet below ground surface 3.0 miles northwest from the stack at Stucky Ridge (see Addendum, Figure 4). There is no basis for ruling out smelter emissions fallout as a source for the arsenic at these depths.

6) *There is no Supportable Rationale in the CDM Report for Expanding the Boundary of the DWAOC.*

There is overwhelming evidence of extensive hydrothermal alteration (with natural arsenic mineralization) reported by MBMG in the Crackerville (SH) and Fairmont (FR) research cores. Based on this evidence and the other technical inadequacies in the CDM Report discussed above there is no justification for expanding the southeastern boundary of the domestic well program-especially into and beyond the known Fairmont and Crackerville geothermally-impacted areas.

CDM Smith Response

The presence of natural bedrock sources of arsenic in specific areas (Crackerville Deep, English Gulch and Fairmont Deep) was acknowledged within the CDM Report. However, ground water exceedances in areas with elevated arsenic concentrations in the surface soil that is very leachable (including Fairmont) cannot be attributed solely to bedrock or geothermal sources, based on the existing data. The presence of arsenic-impacted surface soils along the predominant wind direction is consistent with a smelter fallout source to the southwest of Smelter Hill. Absent data from springs/seeps or shallow piezometers or monitoring wells that convincingly demonstrate the absence of smelter impacts to the uppermost ground water, there is no basis for the Agencies to depart from the current CSM conclusions regarding the impacts of smelter fallout on ground water quality.

Atlantic Richfield's proposed 6-mile limit on smelter fallout and subsequent impacts is far too simplistic for a complex climatological, topographical, and hydrogeologic setting such as the one

that exists at the Anaconda Smelter site. The discussion in the Addendum supports this. If drawn on a map (see attached figure from the 2011 ARWW&S OU ROD Amendment), a six-mile radius circle from the stack would pass through and separate the Dutchman High Arsenic Area, where smelter fallout deposition has resulted in surface soils exceeding 1,000 mg/kg arsenic and impacted shallow ground water, into a Dutchman Smelter-Impacted High Arsenic Area to the southwest and a Dutchman Geothermal-Impacted High Arsenic Area to the northeast. The existing site characterization as shown in the 2011, delineated in large part through piezometer and spring/seep data, shows a trend of arsenic concentrations in ground water decreasing away from the stack until concentrations are below the 10 µg/L standard. The extent of the groundwater plume is more likely defined by aerial arsenic deposition influenced by topography and prevailing wind directions, rather than an arbitrary boundary derived from the flawed statistical interpretation of a limited data set.

References Cited

Field, C.W.; Zhang, L.; Dilles, J.H.; Rye, Robert O.; and Reed, M.H. 2005. "Sulfur and oxygen isotopic record in sulfate and sulfide minerals of early, deep, pre-Main Stage porphyry Cu–Mo and late Main Stage base-metal mineral deposits, Butte district, Montana" *Chemical Geology* 215 (2005) 61-93.